The influence of calcium nitrate on setting and hardening rate of Portland cement concrete at different temperatures

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Abstract. Calcium nitrate in mortars and concrete is used as a multifunctional additive: as set accelerator, plasticizer, long term strength enhancer and as antifreeze admixture. Used binding material and the amount of calcium nitrate, affect the characteristics of the concrete mixture and strength of hardened concrete. The setting time of the initial and the final binding at different temperatures of hardening (+ 20 ˚C and + 5 ˚C) of the pastes made of different cements (Portland cement CEM I 42.5 R and Portland limestone cement CEM II/A-LL 42.5 R) and various amounts of calcium nitrate from 1 % until 3 % were investigated. The effect of calcium nitrate on technological characteristics of concrete mixture (the consistency of the mixture, the density, and the amount of air in the mixture), on early concrete strength after 2 and 7 days, as well as on standard concrete strength after 28 days at different temperatures (at + 20 ˚C and + 5 ˚C) were analysed.

1. Introduction

The main problem is making concrete in winter conditions when atmospheric temperature is below 0 ˚C, which reduces final properties of hardened concrete. Antifreeze admixtures are chemicals which are added to the water when mixing concrete in order to lower the freezing point of the aqueous solution. [1]. These are sometimes considered as accelerate admixtures, the main action of that is to accelerate the hydration of cement as conventional accelerators [2].

Technical calcium nitrate is used as an admixture for concrete production in some countries [3, 4]. The calcium nitrate can be used for concrete production not only as an antifreeze admixture but it can be used as accelerating admixture [3-5]. The use of accelerators in concrete, provides a shortening of setting time or an increase in development of early strength [6,7]. Calcium nitrate is a multifunctional admixture for concrete [8].

Cations and anions increase the setting times of calcium aluminate cements in this case:

Cations: Li^+ « Na^+ < control < $K^+ \leq Ca^{2+} < Mg^{2+} < Sr^{2+} < NH_4^+$

Anions: OH^- « control < $Cl^- < NO_3^- < Br^- < CH_3COO^-$ (acetate) [9].

Calcium chloride, calcium nitride and calcium nitride accelerate hydration process because that have Ca^{2+} cation like cement minerals C_3S and C_2S. In such case crystallization processes are going intensively [1,10].

The research showed that $Ca(NO_3)_2$ is more effective than $CaCl_2$ as the accelerator for hydration of belite (β-C_2S) [2]. This has been confirmed by another researcher who has carried out the research s on technical grade calcium nitrate (including a small amount of ammonium, NH $^{4+}$) [11,12]. The use of accelerators in concrete provides a shorter setting time and an increase in early strength development at the ordinary temperature [1, 13].

Calcium nitrate at relatively high dosages has proven to be an effective inhibitor against chloride induced corrosion of steel reinforcement in concrete [11].

A setting accelerator must give at least 30 min initial setting time at 20 °C, and maximum 60 % of the initial setting time of the reference at 5 °C measured on mortar with equal flow. A hardening accelerator should give 120 % compressive strength compared to the reference after 1 day at 20 °C, and at least 130 % compressive strength compared to the reference after 2 days at 5 °C, as measured on concrete of equal flow. These requirements are presented in the standard [3, 14].

The effectiveness of an admixture depends on such factors as the type and amount of cement, water content, a shape of filling aggregate, gradation and proportions, mixing time, slump, and the temperature of the concrete. Because the efficiency of the calcium nitrate as a set accelerator is strongly dependent on the cement type, the study with 2 different cements types was performed. For these reasons, in the study, fresh 2 different type cements contained calcium nitrate at different curing temperatures (+5, +20 °C) were compared to the results of control sample.

In the present paper, references about accelerators of cement hardening and their impact on properties of the concrete mix and hardened concrete, concrete hardening processes at different temperatures were analysed. The impact of the calcium nitrate on hydration of cement and technological properties of the cement mixes and the early and standard strength of the concrete at different temperatures were tested.

2. Materials and methods for investigation

Two cements were used for the investigation: Portland cement CEM I-42,5R (CEM I R), limestone Portland cement CEM II A-LL 42,5 R (CEM II R) (table 1).

Table 1. The compositions of concrete mixtures.

Cement type	Mark-ing	Compressive strength, MPa		Fineness		C_3S %	C_2S %	C_3A %	C_4AF %
		7 days	38 days	Blaine, cm^2g^{-1}	>90µm				
CEM I 42,5 R	CEM IR	28,9	54,6	3560	1,1	64,6	7,8	6,4	12,8
CEM II A-LL 42,5 R	CEM IIR	29,9	51,1	4400	0,5	58,7	12,9	6,3	10,79

Coarse aggregate with fraction 4/16 mm and sand (0/4 mm) were used for the investigation. Coarse aggregate – gravel meets the requirements of LST EN 12620:2003 [15]. The content of low strength types of rock, such as sandstone, limestone, etc., is not higher than 2 % of mass. Fine aggregate – sand meets the requirements of LST EN 12620:2003 [15]. Water meets the requirements of LST EN 1008:2005 [16].

The setting times of the cement pastes were recorder by an automated 'Vicat' apparatus. The setting time was registered by penetration of a needle with a fixed cross-section and with a constant force into the cement paste. The needle was pressed into the cement paste after 10 minutes. The initial setting time is determined to be when a full depth intrusion of the needle is not obtainable, while the final setting time is taken when the needle no longer penetrates the cement paste at all.

The amount of calcium nitrate was changed from 1 to 3 by weight % of the amount of cement.

The preparation of cement pastes and stirring was carried out at temperature of materials and environment of 20 °C.

At the temperature of 20 °C, the demand of water was determined for cement paste of normal consistency. The need of water for cement CEM I R was 24.6 %, for cement CEM II R– 26.7 %.

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Cement pastes were prepared by mixing them in accordance with EN 196-1. Admixture was dissolved in the water before for paste mixing. Water with admixture was added to the cement. Mixing continued for 120 s at high speed.

All concrete mixtures were mixed in a laboratory. The admixture calcium nitrate was dissolved in the water. At first, dry mixture of cement, fine and coarse aggregate were placed in a laboratory counter-current mixer for 1 min. Then, the calcium nitrate solution for concrete mixtures with calcium nitrate and mixed water for concrete mixtures without calcium nitrate were added into the mixer. The fresh concrete mixtures with and without calcium nitrate admixture were mixed in a laboratory counter-current mixer for a total of 3 min. Concrete mixtures (table 2) with different types of composition were prepared for the investigations. The amount of calcium nitrate was changed from 0.5 to 3 by weight % of the amount of cement. The water / cement ratio in all concrete mixtures was the same. Super plasticizer agent was used of 0.5 % weight for all mixtures because the purpose of this study was to investigate the effects of the calcium nitrate alone.

Table 2. The composition of concrete mixture.

Materials	Amounts of materials in 1 m^3 of concrete mixture
Coarse aggregate, kg	996
Fine aggregate, kg	917
Cement, kg	307
Water, l	168
w/c	0,55
Superplasticizer, kg	1,55

Two methods were used to determine the consistency of the concrete mixture: the slump method and the flow table method.

Concrete mixtures of 10 litres each were prepared for the research. The slump test was done in compliance with the technique set forth in EN 12350-2 [17] and the spread table test complied with EN 12350-5 [18]. 100×100×100 mm specimens moulded from the prepared blend were kept in moulds for 2 days in different conditions (at different temperatures of +20 °C and +5 ˚C) and then for 26 days hardened in water at a temperature of 20 ˚C.

Hardening of concrete specimens were performed in compliance with LST EN 12390–2:2009/P:2011 [19], compression strength – according to LST EN 12390–3[20], and density – according to LST EN 12390-7:2009/P:2011 requirements [21].

3. Results and discussion

Setting time of normal consistency cement pastes was tested at different temperatures: +20 °C and +5 °C. The initial and final setting time of normal consistency pasta binding was determined. Normal consistency cement pastes with different types of cements were tested. The content of admixture was used 0 %,0.5 %, 1 %, 2 %, and 3 %.

It was found out that admixture calcium nitrate was reducing setting time (initial and final) for cement pastes with cements at 20 °C temperature (figure. 1). More effective reduction of initial setting time of cement pastes noticed for the CEM II R cement with a large specific surface (4400 m^2/kg). For the reduction of initial setting time to the 60 % from control paste without admixture (black line in figure 1) dosage of admixture must be more than 2 % for cements CEM I R but more than 1.5 % for cement CEM II R. The reduction of final setting time is more effective in large dosages of admixture. Difference between final and initial setting time is about 50 min in cement pastes without admixture for all cements and about 30 min in cement pastes with 3 % of admixture for all cement. Similar studies were carried out to confirm these results [22]. The scientists studied the impact of $Ca(NO_3)_2$ (0-10 %) amount on setting time of paste of Portland cement with volcanic ash additive. It was observed that an increase in percentage of calcium nitrate ($Ca(NO_3)_2$) reduces the initial and final setting time. This may be attributed to the increase in the concentration of calcium cations. The research showed that by increasing the amount of CN, the initial and final setting time shortens by about 20 %. The other authors also present the same decrease of binding time [23].

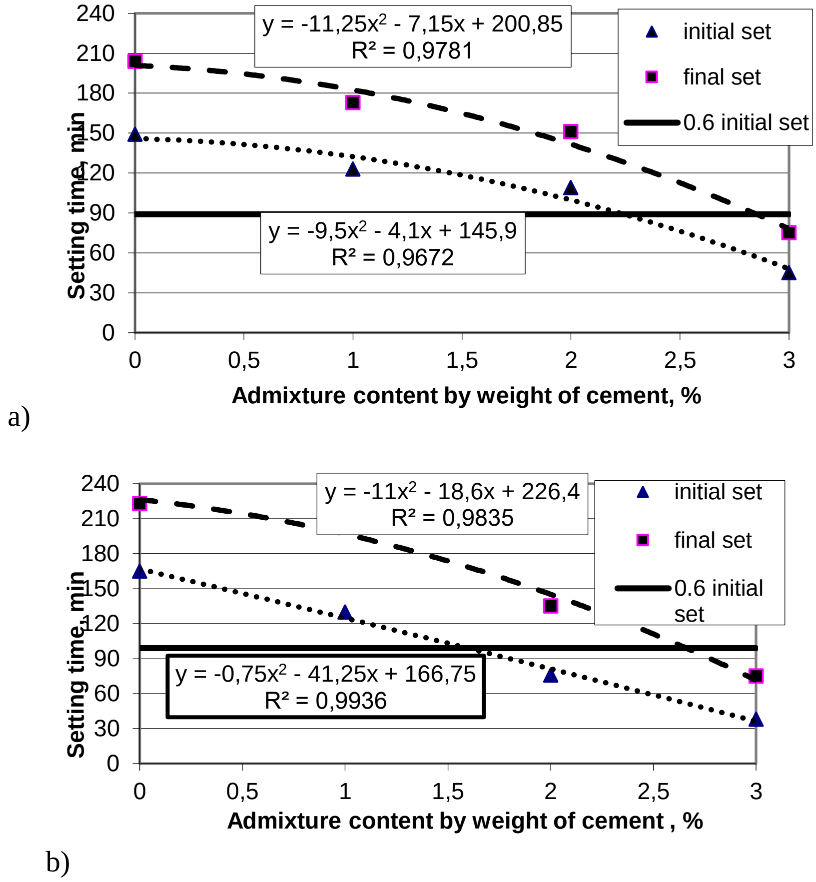


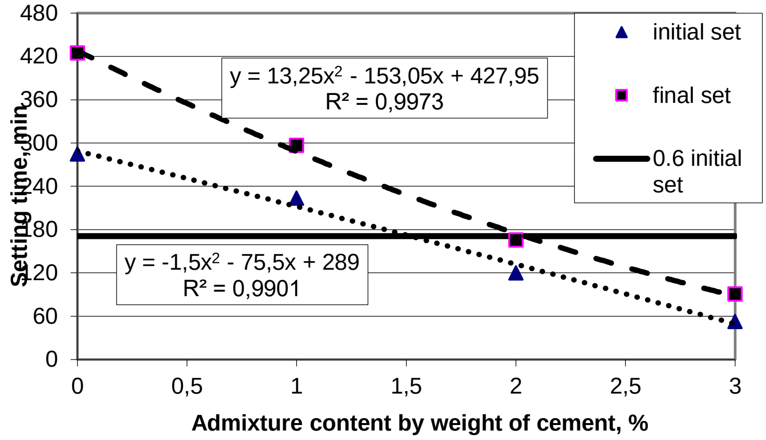
Figure 1. Cement paste setting time at +20 °C temperature (initial and final) vs admixture content with CEM I R cement (a), CEM II R cement (b).

Cement pastes with different cement type and different calcium nitrate admixture content setting time at +5 °C initial and final setting time are presented in the figure 2.

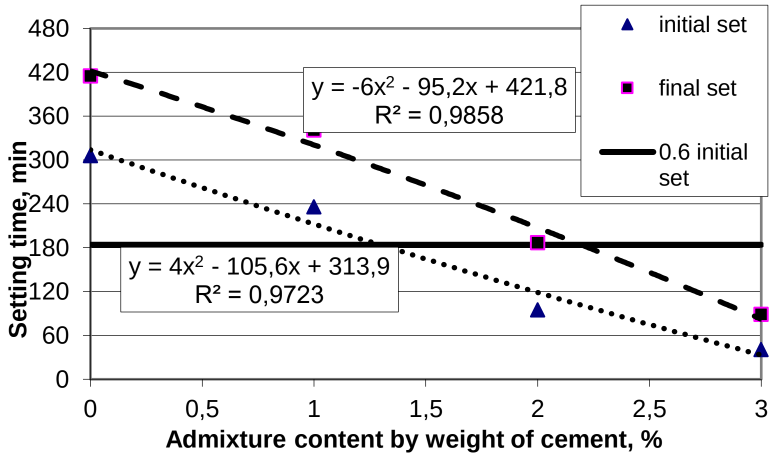
It was found out that the initial and final setting time of cement pastes with all cements increases rapidly with reduction of cement paste curing temperature to +5 °C (figure 2). Initial setting time increases from about 150 min at +20 °C to about 300 min at +5 °C. Final setting time increases from about 210 min at +20 °C to about 420 min in +5 °C. For the reduction of initial setting time to the 60 % from control paste without admixture (black line in figure. 2) dosage of admixture must be more than 1.5 % for cements CEM I R and CEM II R. The reduction of final setting time is more effective in case of large dosages of admixture like for the cement pastes in + 20 °C. The admixture calcium nitrate works like set accelerate more efficiently at +5 °C in comparison with +20 °C.

Measuring of the properties of a concrete mixture was initiated from a slump test. Fluidity of the concrete mix there was determined twice - right after mixing and after 1 hour. The content of calcium nitrate had almost no impact on the consistency after mixing concrete mixture with CEM IR. After one hour, a tendency was observed that with increase of calcium nitrate, dosage consistency of the concrete mix dropped from 12 cm down to 8 cm.

The content of calcium nitrate had minimal impact on the density of the concrete mixture with cement CEM IR. The density of the concrete mixture was ranging from 2376 to 2386 kg/m^3 with difference of 10 kg/m^3.



a)



b)

Figure 2. Cement paste setting time at +5 °C temperature (initial and final) vs admixture content with CEM I R cement (a), CEM II R cement (b).

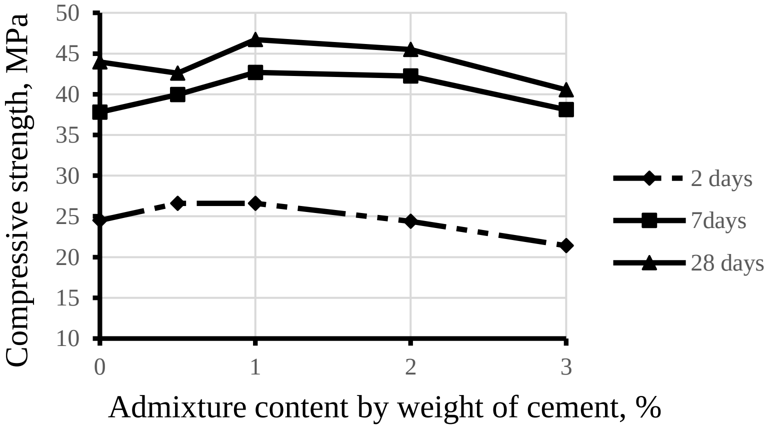
Air content in concrete mixtures with CEM I R ranged from 4.6 % to 5.18 %. The admixture calcium nitrate has minimal influence on the air content in concrete mixture.

Similar tendencies have been observed with limestone Portland cement CEM II R. In this case, by increasing the content of the calcium nitrate, the consistency at the beginning was increasing and reached the highest value, by adding 1 % of CN. After 1 hour, the consistency dropped, however slightly. Without the admixture calcium nitrate, the consistency reached 7.3 cm and after adding 3 % - consistency of the cement mix reached 5.56 cm. In this case the difference is just 1.94 cm. In this case the difference is less compared to the first cement. The same as in the first case it had minimal impact on density of the concrete mixture with CEM II R. In this case the values of density ranged from minimal 2332 kg/m^3 to the maximal 2378 kg/m^3.

Air content in the concrete mixture varied little. Density and air content of the concrete mixture are interrelated. The higher content of air in the mix, the lower density. In this case air content in the mixture ranged from 4.48 % when the mixture contained 1 % of calcium nitrate to 6 % when contained no admixtures at all.

The same tendencies as in the concrete with limestone Portland cement was observed. In this case by increasing the content of the calcium nitrate, the fluidity at the beginning was increasing and reached the highest value, by adding 1 % of calcium nitrate. The values of density ranged from minimal 2331 kg/m^3 to the maximal 2360 kg/m^3. Air volume in the concrete mix varied little.

Compressive strength of concrete sample with different cement type and different calcium nitrate admixture after 2, 7 and 28 days are presented in the figure 3.



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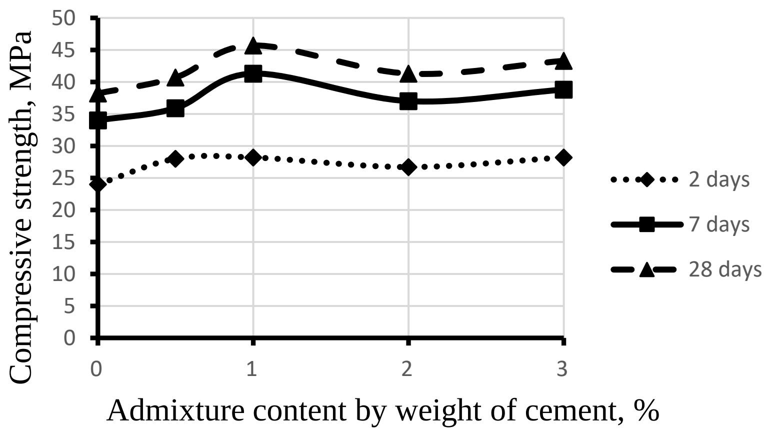


b)

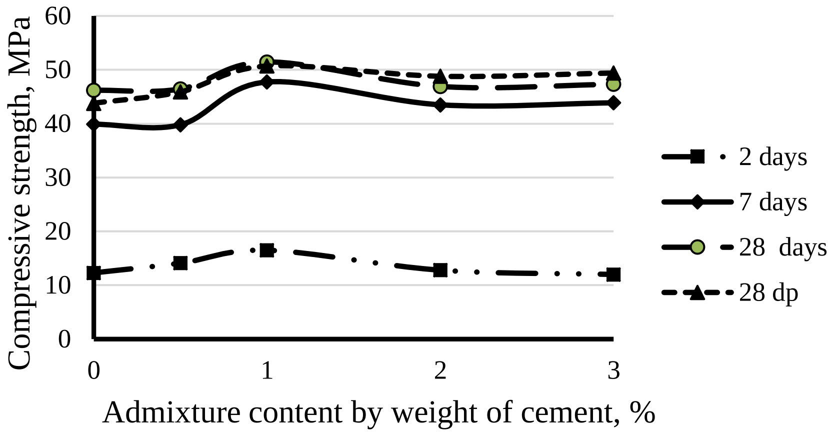
Figure 3. Compressive strength of concrete samples with CEM I R cement (a), CEM II R cement (b) at 20 °C temperature.

Compressive strength of concrete samples increased and reached the highest value, by adding 1% of calcium nitrate for the CEM I R and CEM II R. The same results are observed after 2, 7 and 28 days (figure 1). The researchers, by contrast, found that increase in strength was also recorded as being proportional to the increase in calcium nitrates ($Ca(NO_3)_2$) content [22]. Other researchers also indicate that the compressive strength increases with linear dependency on the CN addition for CEM I [23].

For comparison 28 dp, the specimen in the forms were kept at the temperature of 20 °C for two days and later hardened in water for 26 days (figure 2).

At the temperature of +5 °C addition of calcium nitrate, more than 1 % increases compressive strength of concrete, after 2 days more than 30% for cement CEM I R (figure 4). The concrete with

CEM II R cement compressive strength after 2 days increases by adding 0.5 % of admixture is 37 % and % of admixture is 67 %.



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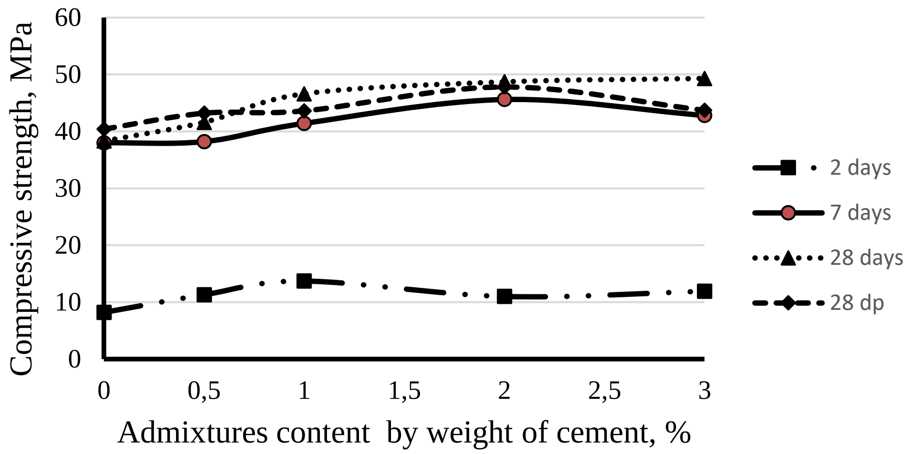

b)

Figure 4 . Compressive strength of concrete samples with CEM I R cement (a), CEM II R cement (b) at 5 °C temperature.

4. Conclusions

Cement pastes and concrete mixtures containing different content of admixture calcium nitrates retain suitable technological properties from 30 to 120 min with dosage of admixture from 0 % to 3 % in different temperatures from +20 ºC to + 5 ºC. Concrete mixtures containing admixture of calcium nitrate can be used for the above-mentioned time depending to the content of calcium nitrate that is restricted by the concreting works temperature.

The admixture of calcium nitrate has no significant influence on slump of concrete mixtures after mixing and after 1 hour. The admixture of calcium nitrate has minimal significant impact on air content in the concrete mixture.

The calcium nitrate increases the early strength of the concrete mixes at temperature of +5 °C. The calcium nitrate increases early strength of concrete after 2 days more than 30 % for CEM I R and CEM II R.

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